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OFFICE OF NAVAL RESEARCH

R&T Project Code 413 a 001

Contract No. N00014-89-J-1235

Technical Report No. 11



Spectroscopy and Reactions of Hydrazoic Acid on
Silicon Single Crystal Surfaces (III).

HN₃ and DN₃ on Si(111)-7x7

by

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Prepared for Publication

in the

Surface Science

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Abstract

We have studied the thermal stability and spectroscopy of HN_3 on $\text{Si}(111)\text{-}7\times 7$ in the temperature range from 120 to 1350 K. The results are similar to those observed on other two low-index Si surfaces. HN_3 was found to molecularly adsorb on $\text{Si}(111)\text{-}7\times 7$ at 120 K, with the formation of dimers at higher dosages (≥ 2.0 L). At 270 K, HN_3 began to decompose into HN and N_2 species as indicated by the changes in the NH vibration mode in HREELS and the chemical shift of N 1s XPS peak. Between 300 and 800 K, the NH species further decomposed into H and N on the surface, while N_2 desorbed molecularly. In this temperature range, the steady increase of the SiN_x and Si-H peaks were noted and LEED exhibited a weak (1x1) pattern.

When the surface was annealed at $T_s > 800$ K, H(a) recombined to desorb, with N remained as the only species on the surface. Further annealing at higher temperatures caused the gradual transformation of the SiN_x species into Si_3N_4 , as confirmed by all the spectroscopic results, including LEED which showed an (8x8) pattern.

1. INTRODUCTION

The interaction of N-containing compounds with silicon surfaces has attracted much attention over the past two decades. The reason for these studies is to better understand the mechanisms for the formation of silicon nitride films, which are important in microelectronic industries. Silicon nitride can be used as an insulation and passivation layer for very large-scale integrated (VLSI) circuits [1-3] as well as high temperature structure ceramics [4,5].

Since NH_3 is one of the most popular sources for nitridation, a great deal of research has been performed on its reactivity on silicon single crystals under ultra high vacuum (UHV) conditions [6-16]. By means of different spectroscopic methods, it is now understood that ammonia was dissociatively adsorbed on silicon surfaces at relatively low temperature (~ 80 K). The most interesting features about the mechanism is that its reaction behavior upon annealing depends strongly on the nature of the silicon surface. For example, on $\text{Si}(111)\text{-}7\times 7$, both NH_2 and NH have been observed at elevated temperatures; however, no NH was found at any temperature on the $\text{Si}(100)\text{-}2\times 1$ surface. It is believed that the dangling bonds on different surfaces play a very important role in the subsequent reactions [15].

However, despite the convenience of ammonia as a source for silicon nitride, it requires a high operational temperature in order to have a good quality film. To lower the required temperature (>1300

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K), alternative N sources have been used; these include N [17], NO [18], N_2H_4 [19] as well as hydrazoic acid (HN_3) [20-22]. By using HN_3 and O_3 , Ishihara et al. [22] have successfully demonstrated the production of silicon nitride films at temperatures around 700 K, which was much lower than that required with NH_3 . Other wide bandgap semiconductors like GaN and BN have also been synthesized by using hydrazoic acid as a nitrogen source [23, 24]. Though HN_3 has proved to be a good nitrogen source for the nitridation process, its reaction mechanisms on semiconductor surfaces remain unclear and need to be addressed.

As an extension of our recent studies to elucidate the mechanisms of HN_3 reaction on silicon surfaces [20,21], in this work we investigate the reaction of $\text{HN}_3(\text{DN}_3)$ on the Si(111)-7x7 surface in the temperature range 120-1350 K. By utilizing different surface analysis techniques: AES (Auger Spectroscopy), LEED (Low Energy Electron Diffraction), XPS (X-ray Photoelectron Spectroscopy), UPS (Ultra-violet Photoelectron Spectroscopy) and HREELS (High Resolution Electron Energy Loss Spectroscopy), we are able to monitor the interaction of $\text{HN}_3(\text{DN}_3)$ with the Si surface under varying experimental conditions. The results obtained for the Si(111) surface reaction are briefly compared with those obtained from two other low Miller index Si crystals.

2. Experimental

The experiment was carried out in a stainless steel UHV system with a base pressure of $< 2 \times 10^{-10}$ torr. The system, which has been equipped with multiple surface analysis tools, was constructed in order to transfer sample from ambient into the chamber in a few minutes without disturbing the UHV condition. A description of the setup can be found elsewhere [20,21,25,26].

AES analysis was performed by using a 2 KV primary electron-beam and the spectra were recorded in the first derivative mode. A reverse-view LEED optics was used to characterize the surface structure. For HREELS measurements, a 5-eV primary beam with a resolution of 8 meV FWHM (Full Width at Half Maximum) in the straight through mode was employed. Off-specular EELS spectra were recorded by rotating the energy analyzer around the axis perpendicular to the incident beam. A monochromatic Al $K\alpha$ (1486.6 eV) light source was used for XPS experiments; peak positions were calibrated with the clean Si 2P peak (K.E.=1386.0 eV). Helium discharged lamp provided the 40.8 eV (He II) photons needed for the UPS study.

A large Si(111) crystal (B-doped, 10 Ω -cm resistivity) from the Virginia Semiconductor Co. was cut into 1.5 \times 1.0 cm² samples. The samples were chemically cleaned with 5% HF solution, and rinsed with deionized water. After the dried sample was introduced into the UHV chamber, it was annealed at $T_s > 1500$ K until no contaminants

such as C, N, and O could be detected by XPS and AES or HREELS. The cleaned Si(111) sample displayed a sharp 7x7 LEED pattern.

Both HN_3 and DN_3 were prepared in the same way as previously reported [20], dried NaN_3 was allowed to react in vacuo with $\text{H}_3\text{PO}_4(\text{D}_3\text{PO}_4)$ to produce the hydrazoic acid. The gaseous acid product was further purified by trap-to-trap distillation using dry ice and liquid N_2 traps. FTIR analyses showed very pure HN_3 and DN_3 with a high D-enrichment [20]. The $\text{HN}_3(\text{DN}_3)$ was stored at dry ice temperature to prevent decomposition before experiment. The gases were leaked into the UHV system through a 1/8 inch stainless steel tubing after repeated purging and passivation of the inlet line.

3. Result and Discussion

3.1 AES and LEED

Figure 1 shows the dependence of the Si and N AES signals on the dosage of HN_3 on Si(111)-7x7 at 120 K. All peaks were normalized to the clean Si LVV AES line at 92 eV. This plot clearly shows that the saturation occurred at about 9.0 ± 2.0 L ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr}\cdot\text{s}$). Similar results were also observed by Jonathan et al [27] for HN_3 on Si(100)-2x1 at room temperature.

Figure 2 shows the temperature effect on the AES signal intensities for a 6.0 ± 1.0 L HN_3 dosed surface. All spectra were recorded by annealing the surface at the indicated temperatures for 2 minutes and then cooling down to 120 K for 5 minutes. The clean Si(111) surface showed a Si LVV peak at 92 eV and its LEED exhibited a sharp 7x7 pattern. When 6 ± 1.0 L HN_3 was dosed on the

surface, the 92 eV peak intensity decreased by about 35% and a new peak corresponding to N KLL appeared at 380 eV. A hump centered at 84 eV was also observed; according to Delord et al [18], it is due to Si LVV after the bond formation between the silicon and the nitrogen atoms. Meanwhile, LEED displayed a "flower" pattern, having 1x1 spots surrounded by the 1/7th-order spots, which has also been observed for halogen atoms on Si(111)-7x7 [28,29]. This could be explained as the (7x7) structure being locally destroyed by the presence of HN_3 , so the long range two dimension (7x7) pattern no longer exists.

In the entire temperature range of $270 \text{ K} < T_s < 1000 \text{ K}$, the Si LVV and the N KLL peak positions remained essentially the same, but the 92 and 84 eV peaks became better resolved. The LEED pattern changed from the flower pattern to a weak 1x1 pattern at $T_s > 615 \text{ K}$. The observed changes can be attributed to the dissociation of HN_3 on the surface. As the surface was annealed at 1200 K, the AES spectrum well resembles other high temperature Si-nitridation results [18,30]; both the nitrogen enhanced Si LVV peak at 84 eV and the N KLL peak at 375 eV were clearly observed. The LEED showed a strong 8x8 pattern, which was observed earlier in the Si(111) nitridation processes [10,17,18]. This 8x8 pattern is believed to be an overlapped lattice constructed by two different surfaces, Si(111)-1x1 and a 8/11 length unit cell of Si(111)-1x1 lattices [17].

3.2. HREELS

Figures 3 and 4 show the HREELS results of a 2.0 ± 0.5 L HN_3 dosed Si(111)-7x7 surface at 120 K and then annealed at the indicated temperatures. At 120 K, peaks at 56, 77, 150, 165, 270 meV and humps at 395 and 414 meV were observed. By analogy to the HN_3 IR/Raman spectra [31,32] and HREELS measurements for HN_3 on both Si(110) [20] and Si(100) [21], these peaks can be assigned to the individual vibrational modes as listed in Table 1. According to Pimentel et al. [32], the 56 and 395 meV peaks can be attributed to the torsional and the stretching vibrations of the hydrogen-bonded NH of the HN_3 dimers, respectively. Thus, the observed peaks at 56 and 395 meV allow us to conclude that at $T_s=120$ K and 2.0 ± 0.5 L dosage, HN_3 molecularly adsorbed with partial formation of dimers on the Si(111)-7x7 surface.

As the surface was warmed to 270 K, all peak intensities decreased by more than 2 times, especially the torsional vibration (56 meV) and the NH stretching (394 meV) vibration of the hydrogen-bonded NH of $(\text{HN}_3)_2$. This indicates the breaking of the dimers into the monomers and the partial desorption of HN_3 . At the same time, the NNN symmetric stretching vibrational peak at 150 meV was attenuated and a new peak at 90 meV due to various Si and N bonding in SiN_x ($x=1,2,3$) [33-35] appeared. These observations suggest some dissociation of HN_3 into HN and N_2 species as well. The partial cracking of the HN-NN bond is also indicated by the shifting of the broad NH stretching vibration peak to 418 meV due to the partial

contribution from the NH species on the surface. Interestingly, in contrast to the case of $\text{HN}_3/\text{Si}(100)$, no N_2 vibrational mode at 190 meV could be clearly identified at this temperature. However, the possibility of the N_2 triple bond stretching vibrational mode (~ 270 meV) cannot be ruled out, as will be discussed further shortly.

When the surface was annealed at 560 K, the NH (165 meV) bending vibrational mode essentially vanished and the SiN_x stretching vibration peak shifted to 100 meV. Meanwhile, the N_3 asymmetric stretching vibrational peak (270 meV) decreased in intensity and broadened in FWHM. The broadening of the 270 meV peak is due to the partial contribution from the Si-H stretching vibration expected at 258 meV and the possible N_2 triple bond stretching vibrational mode. In addition, the NH stretching vibration also shifted from 418 meV to 423 meV. Thus, the HREELS results at 560 K suggest a substantial breaking of the HN-NN bond as well as some cleavage of the N-H bonds.

At $T_s=615$ K, the 100 meV peak shifted to 110 meV and a new peak at 50 meV could be resolved. The 270 meV peak was further attenuated and broadened, probably due to the continuous formation of the Si-H species, which should show a vibrational peak at ~ 260 meV [36]. It was noted that at this temperature, the intensity of the 270 meV peak became weaker, suggesting that more residual N_2 desorbed from the surface. This observation is also consistent with the result of a TPD study of HN_3 on $\text{Si}(100)\text{-}2\times 1$ [27], in which a second peak at 620 K due to N_2 desorption was observed. Additionally, a barely visible hump at 190 meV could be attributed to

the N=N double bond stretching vibration, which was better resolved in the case of HN₃ on Si(100).

When the surface was annealed at temperatures between 700 to 1000 K, dramatic changes occurred in the spectrum. The NH stretching mode (422 meV) gradually disappeared due to the complete breaking of the N-H bond. This was also indicated by the increasing of the Si-H peak (264 meV) at 800 K, which then vanished at 1000 K due to the desorption of H from the surface. This finding has also been reported by other groups for the NH₃ on Si(111) [9,15]. These observations obviously suggest that at $700\text{ K} < T_s < 1000\text{ K}$, the HN_(a) further dissociates into N and H; the latter leaves the surface as H_{2(g)}, while the N species left on the surface forming various types of bonds with silicon as indicated by the broadening and the shifting to higher energy of the SiN_x peak.

Finally, at 1330 K the broad peak at ~130 meV splitted into 4 peaks at 60, 95, 130 and 145 meV, which correlate well with the IR/Raman [37] and the HREELS [9, 38] results taken from silicon nitride (Si₃N₄), indicating the formation of Si₃N₄ on the surface at this temperature.

Figures 5 and 6 display the HREELS results of a 2.0 ± 0.5 L DN₃ dosed Si(111)-7x7. At 100 K, peaks at 60, 125, 150, 270, and a shoulder at 300 meV due to the molecularly adsorbed DN₃ were observed. All peak assignments were also listed in Table 1. In addition to these peaks, the corresponding HN₃ peaks were also observed in the 100 K spectrum. The HN₃ peaks resulted from the

fast H-for-D isotope exchange occurring in the dosing line and on the wall of the system. The effects of thermal annealing on the ELS of DN₃ were essentially the same as those of HN₃. However, the spectra were more complicated due to the co-existence of the corresponding HN₃ vibrational modes. Similar to HN₃, the DN₃ began to dissociate at 250 K; both the NNN (150 meV) symmetric stretching vibration and the in-plane D-N (125 meV) bending peak diminished and then disappeared at 610 K. At higher temperatures, only the N atoms remained on the surface.

3.3. XPS

Figure 7 shows the temperature dependence of N1s XPS results for a 2.0 ± 0.5 L HN₃ dosed Si(111)-7x7 surface. At 120 K, two peaks located at 400.3 and 404.1 eV having FWHM of 2.5 and 1.7 eV, respectively, were observed. These features agreed well with both the *ab initio* SCF MO calculation [39] and the XPS results taken from solid HN₃ [40]. The higher binding energy peak at 404.1 eV was due to the central N atom (II), while the broader 400.3 eV peak due to the combination of the two terminal N atoms (I and III), in the HN₃ molecule as shown in fig. 8. The latter peak can be deconvoluted into two peaks with equal intensities, same FWHM and an energy separation of 1.0 eV, located at 400.8 and 399.8 eV [21]. According to the atomic charge calculation [40], these two peaks are due to N_{III} and N_I, respectively. The small shoulder at around 397.5 eV could be attributed to the trace of atomic nitrogen or the NH species formed on the surface. The latter, derived from the dissociative adsorption HN₃, is believed to be more plausible.

When warmed to 270 K, all peak intensities were attenuated by about three times and shifted by 0.5 eV to the lower B.E. side with same peak-to-peak separation, except the peak at 397.5 eV, which actually grew a little. This is indicative of a partial desorption and an additional decomposition of HN_3 into HN and N_2 as well. Earlier, Boszo et al. [13] reported that the N 1s XPS for imide on Si(111)-7x7 surface ($\text{Si}_2=\text{N-H}$) located at 398.0 eV. This peak would overlap with the corresponding HN_3 peaks.

When the surface was annealed at 640 K, molecular HN_3 peaks disappeared, and the 397.5 eV peak due to NH and/or the atomic nitrogen on silicon surfaces [11-13] dominated the spectrum. On the other hand, the unsymmetrical peak shape at high B.E. side of the XPS spectrum indicated the remaining of some NH species. These observations are consistent with our HREELS results. As the temperature reached 800 K, the N XPS was at about the same position as that at 640 K, with its FWHM being reduced by 15%, due mainly to the further dissociation of the NH species. Finally at 1180 K, the N 1s peak shifted to 397.6 eV with noticeable broadening in FWHM, due to different bondings between N and Si. Similar effect was also reported by Kubler et al. [6,7] for NH_3 on silicon surfaces.

3.4. UPS

Figure 9 shows the UPS results taken from a 2.0 ± 0.5 L HN_3 dosed Si(111)7x7 surface. The bottom spectrum represents a clean Si(111)-7x7 surface, where S_1 and S_2 surface states [41] at 0.2 and 0.8 eV can be clearly resolved. After dosing 2.0 ± 0.5 L HN_3 at 120 K, these surface states disappeared, indicating that HN_3 interact with the surface through the silicon dangling bonds. In addition, peaks at 4.7, 6.0, 9.8 and 13.5 eV below E_F were clearly observed. By analogy to the gaseous HN_3 UPS (He I and He II) [40,42] results, the peaks at 4.7 and 6.0 eV could be assigned to the non-bonding $2a''$ and $9a'$ orbitals associated with the N-H group; the broad peak centered at ~ 9.8 eV resulted from the overlap of the $8a'$, $7a'$ and $1a''$ orbitals, due to the combination of the bonding $p\sigma$ and π orbitals; the low intensity peak at 13.5 eV, which is not visible in the He I spectrum, could be assigned the $6a'$ ($s\sigma$) bonding orbital associated with the N-H bond. The broadening of the 9.8 eV peak may also be caused by the partial formation of the dimers on the surface as clearly shown in our HREELS results for the interaction between HN_3 molecules and the surface. The latter could also explain the differences observed for HN_3 on Si substrates and gaseous HN_3 UPS spectra.

As the sample was warmed to 270 K, all peak intensities were attenuated to some extents indicating the partial desorption of HN_3 , as also indicated by the results from other measurements. The stronger attenuation of the peaks at 4.7 and 6.0 eV, the broadening of the 4.7 eV peak and the growth of the peak at ~ 7.0 eV due to the Si-N bond

evidently suggest that the dissociation of HN-NN bond also occurred at this temperature. In addition, the broad peak at 9.8 eV separated into two peaks at 9.0 and 10.3 eV, they can be attributed to the 8a' and the indiscernible 7a' and 1a', respectively. Thus, probably reflects the breakup of the HN₃ dimers.

Further annealing of the surface to higher temperatures caused the further cracking of the HN-N₂ bond as the spectra was gradually dominated by the broad peak at ~7 eV with two shoulders at ~4 and 10 eV, respectively, due to the formation of the Si nitride. The continuous decrease of the 13.5 eV peak, on the other hand, indicates the dissociation of the N-H bond. Finally at 1180 K, the spectrum having peaks at 4.2 and 6.6 eV with a tail extended to 13 eV was very similar to those taken from Si₃N₄ samples [11,43].

4. Summary

By using four different electron spectroscopies, we were able to determine that the hydrazoic acid (HN₃) was primarily molecularly absorbed on all three silicon single crystal surfaces at 120 K. At dosage higher than 2.0 L, HN₃ started to form dimers on the surface [32] as indicated in the HREEL results.

After warming the sample to 270 K, the HN₃ began to desorb as well as to decompose into NH(a) and N₂(a) on all three surfaces. This dissociation reaction is an energetically favored pathway comparing with the formation of H and N₃ species [44]. The HN-NN bond breaking is indicated by the attenuation of the bending mode of N₃ (155 meV), the growth of the SiN_x peak (~90 meV) and the shifting of

the NH stretching peak to 418 meV in HREEL spectra; this is also indicated by the observed strong attenuation of the 6.0 eV peak and the growth of the 7.0 eV peak in UPS at the same temperature.

However, the N₂ binding states could be different on three surfaces. Figure 10 compares the EELS of HN₃ on Si(111)-7x7 and Si(100)-2x1 at a similar dosage and temperatures. A shoulder at 190 meV appeared on Si(100)-2x1 but not on Si(111)-7x7 at 270 K. According to the HREELS studies of N₂ on the different surfaces [45,46], the adsorbed N₂ showed vibrational frequencies ranging from 190 meV to 270 meV. Although previous study [47] suggested that N₂ can hardly react with the silicon surfaces at room temperature, Jonathan et al. [22] have indicated that N₂ species produced from HN₃ decomposition on Si(100)-2x1 remained on the surface at temperatures ≥ 500 K. Thus the observed 190 meV peak in EELS for HN₃ on Si(100)-2x1 at 270 K could be attributed to the stretching vibrational mode for N₂ adsorbed on the surface.

Between $270\text{ K} < T_s \leq 800\text{ K}$, the continuous intensity decrease of the N₃ bending vibration at 165 meV and the gradual shift of the SiN_x ($x=1,2,3$) vibrational mode from 90 to 100 meV indicated a substantial dissociation of HN₃ into HN and N₂. In this temperature range, the ~7.0 eV peak due to Si-N bond in UPS [43] gradually became the dominant feature and the N_{1s} XPS peak changed from multiple peaks to a single peak at 397.5 eV.

At temperatures higher than 800 K, the further decomposition of the NH into the H(a) and N(a) species essentially completed on all

three surfaces. The H(a) species recombined to form H₂ and desorbed from the surface at T_s > 800 K as indicated by the disappearance of the Si-H peak at 265 meV in HREELS, while the N species left on the surface forming Si nitride.

It is worth mentioning that at high temperatures, UPS data showed some differences for HN₃ on Si(111)-7x7 and on the other two silicon surfaces. For Si(111)-7x7 (bottom of fig.11), a strong N₂p peaks at 6.5 eV below E_F was observed in the 1190 K spectrum; whereas for Si(100)-2x1 (top of fig.11) and Si(110) [20], the UPS results were similar to those of the clean surfaces. This difference, according to previous nitridation studies [12,38], is probably due to the penetration of nitrogen atoms into the Si(100) and Si (110) subsurfaces at higher temperatures. Finally, the 1350 K HREEL spectra for all three surfaces closely resembled those known vibrational spectra of Si₃N₄ [9,37,38].

The mechanism for the HN₃ reaction on these low Miller-index silicon surfaces can be summarized as follows:

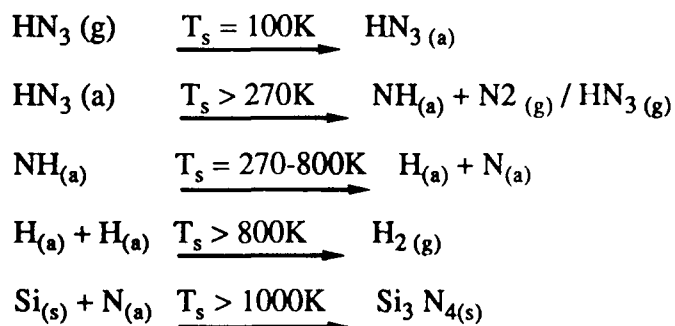


Table 1. Vibrational Frequencies (in meV) and assignments of HN₃ and DN₃ in the gas phase and on the silicon surfaces.

Vibrational Mode	Gas Phase ^(a)		Si(111)-7x7		Si(100)-2x1 ^(b)		Si(110) ^(c)	
	HN ₃	DN ₃	HN ₃	DN ₃	HN ₃	DN ₃	HN ₃	DN ₃
$\delta_a(\text{NNN})$	66	61	56	60	56	60	55	---
$\delta_s(\text{NNN})$	75	73	77	---	73	---	77	73
$\nu_s(\text{NNN})$	143	147	150	151	153	153	150	158
$\delta_a(\text{HN})$	157	118	165	125	163	128	160	128
$\nu_a(\text{NNN})$	265	262	270	270	267	271	265	270
$\nu_s(\text{NH})$	414	307	414	300	415	300	414	307

(a)Ref. 26. (b)Ref. 20. (c)Ref. 21.

Acknowledgement

The authors gratefully acknowledge the support of this work by the Office of Naval Research under contract No. N00014-89-J-1235

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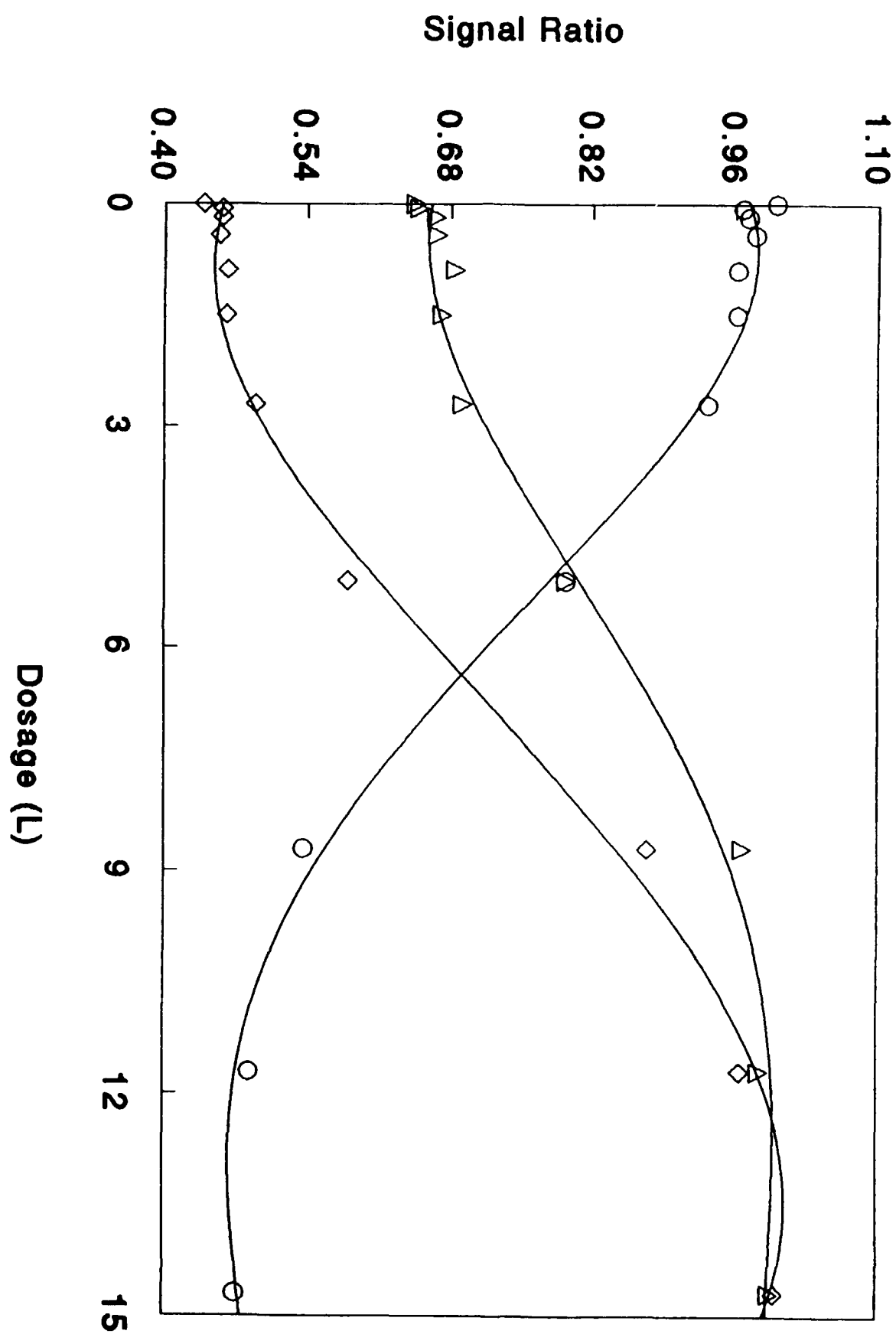
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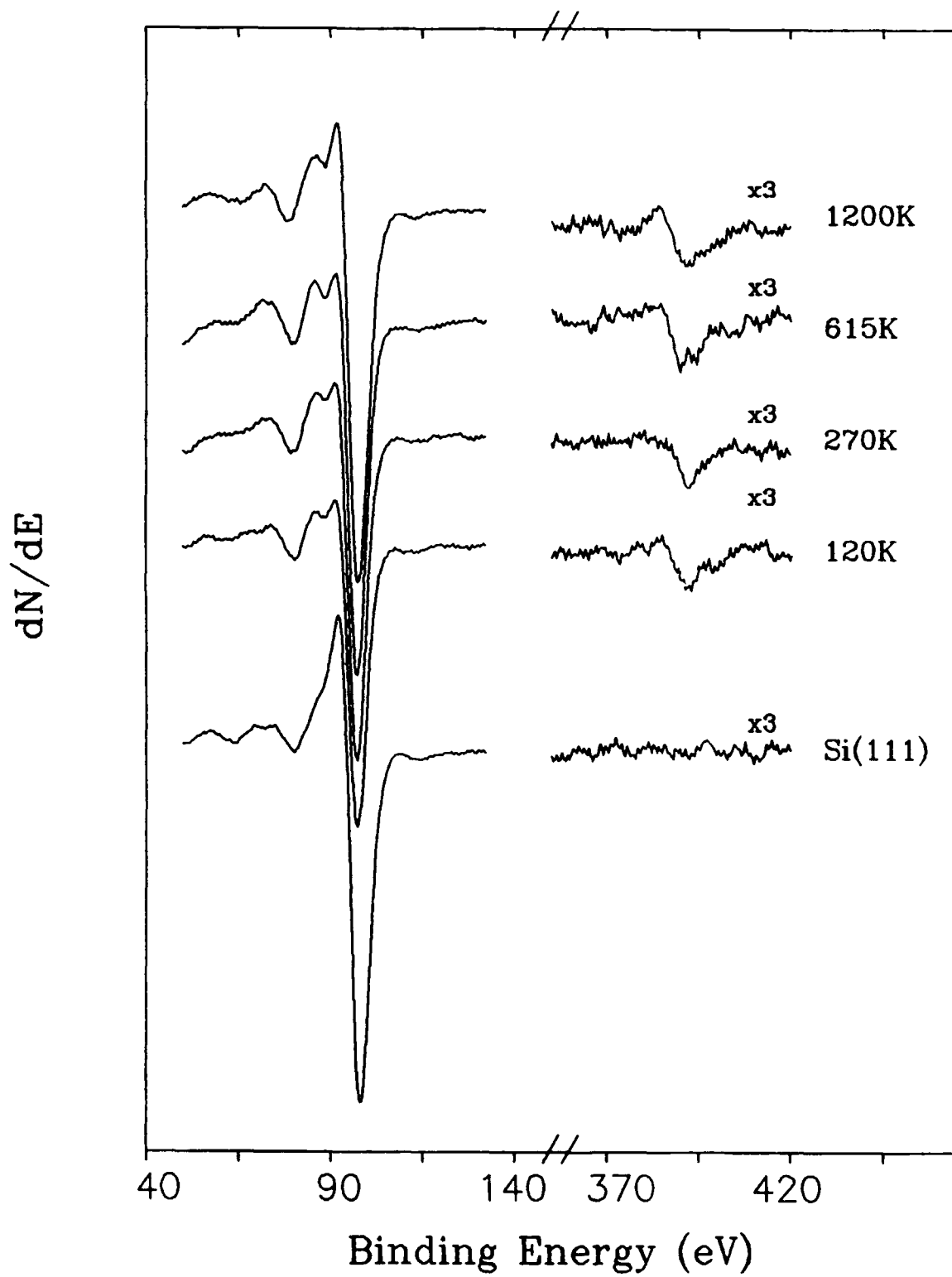
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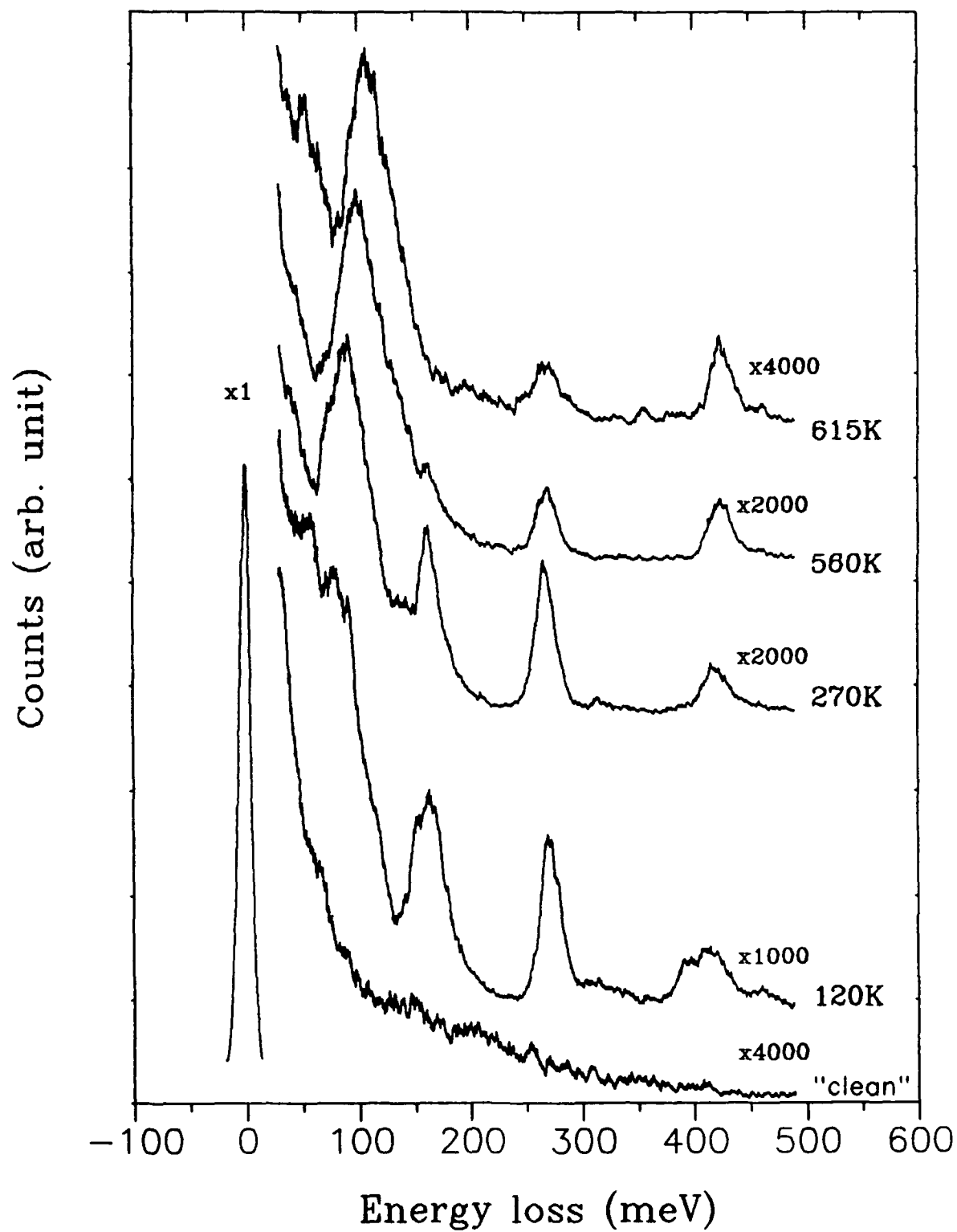
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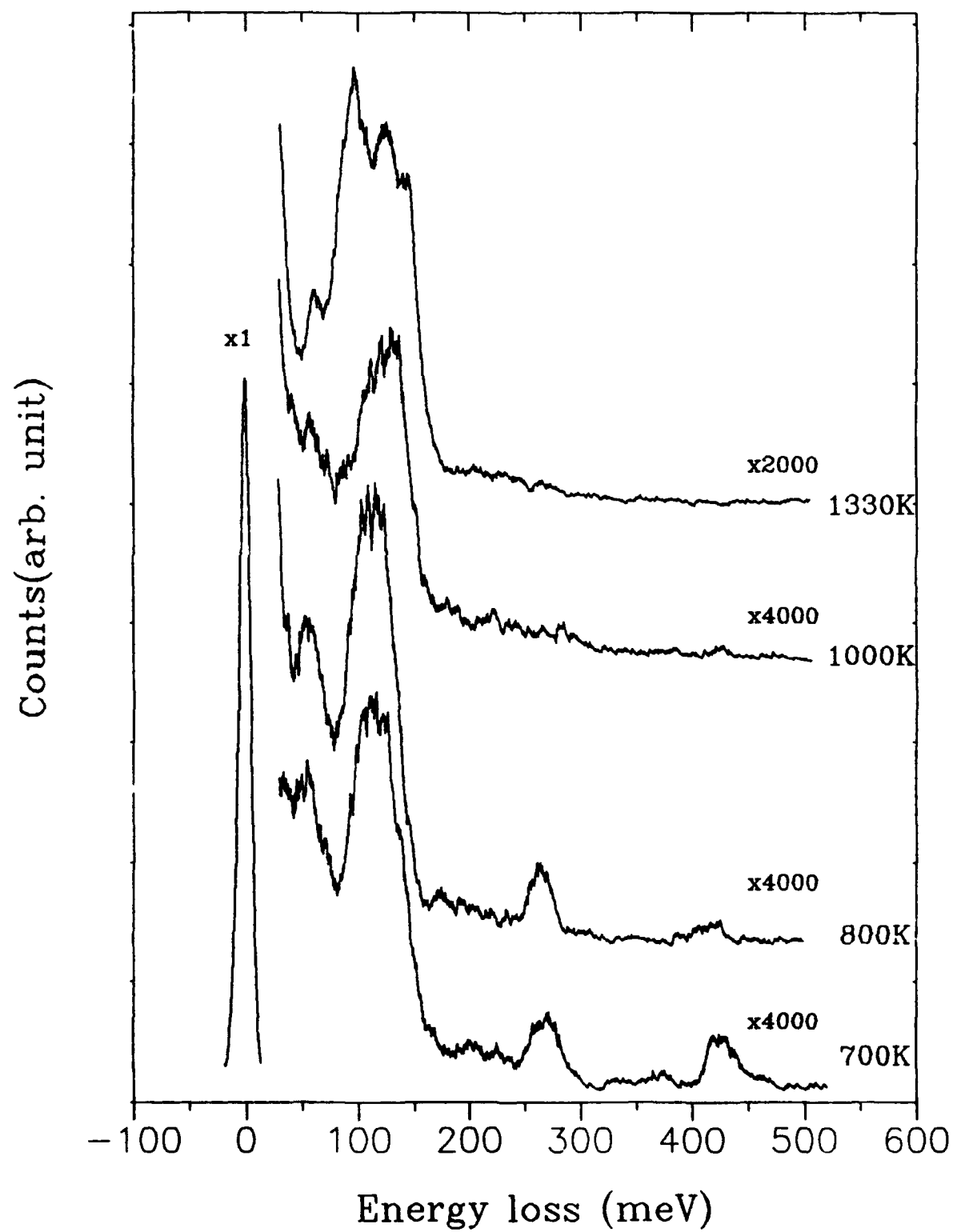
Captions

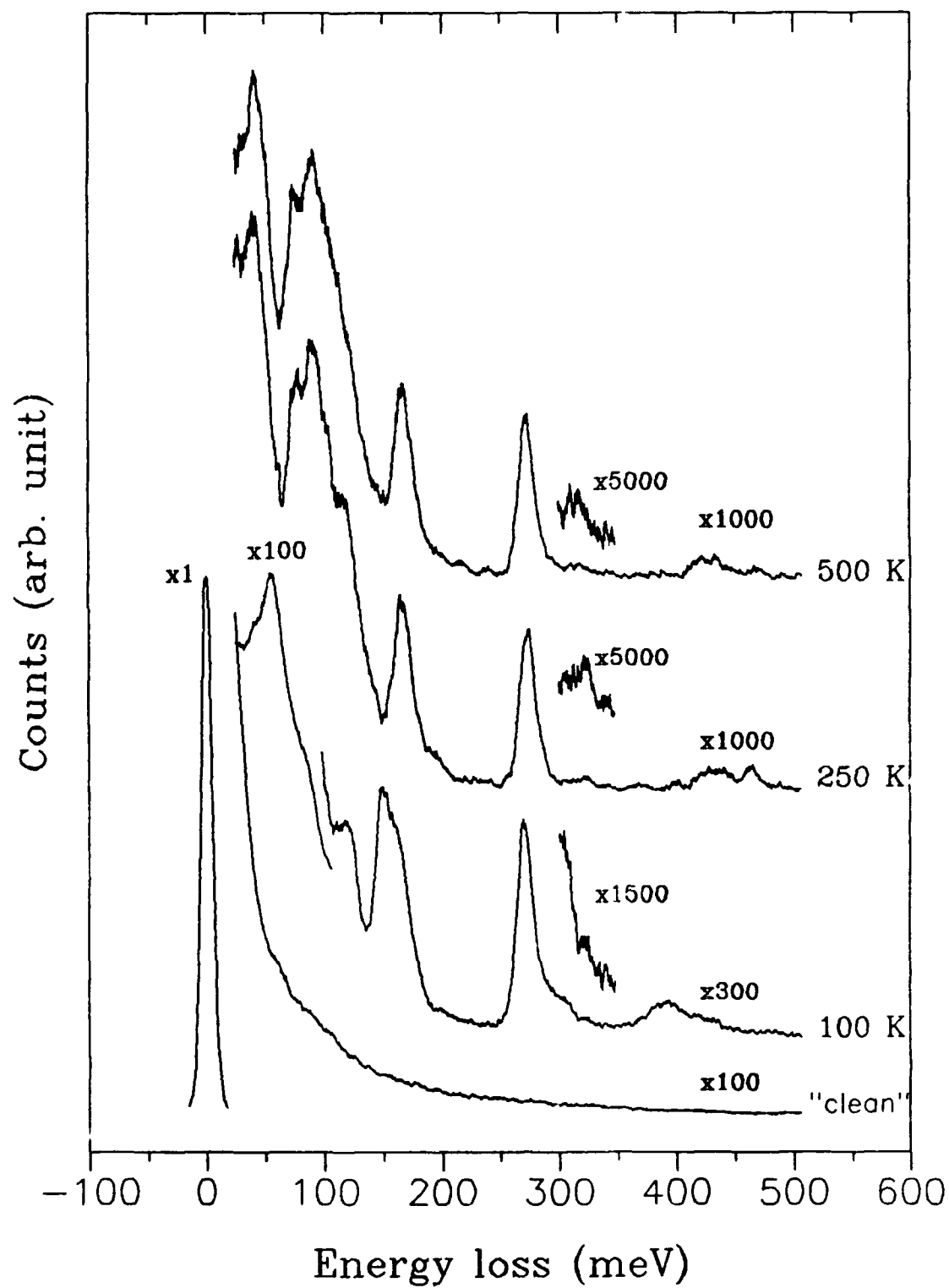
- Figure 1. Dosage dependence of the AES signal intensity for HN_3 on $\text{Si}(111)\text{-}7\times 7$ at $T_s=120$ K, intensities of Si LVV (open circle), nitrogen enhanced Si LVV (open triangle) and N KLL (open square) were normalized to the clean Si LVV peak at 120 K.
- Figure 2. Temperature dependence of the AES signal from a 6.0 ± 1.0 L HN_3 dosed $\text{Si}(111)\text{-}7\times 7$ surface. Note that the Auger peaks were taken in the first derivative mode.
- Figure 3. HREELS of 2.0 ± 0.5 L HN_3 dosed on $\text{Si}(111)\text{-}7\times 7$ at 120 K then annealed to the indicated temperatures. All spectra were recorded at a primary energy of 5.0 eV.
- Figure 4. Same as Figure 3 for different temperatures.
- Figure 5. HREELS of 2.0 ± 0.5 L DN_3 dosed on $\text{Si}(111)\text{-}7\times 7$ at 100 K then annealed to the indicated temperatures.
- Figure 6. Same as Figure 5 for different temperatures.
- Figure 7. N 1s XPS of 2.0 ± 0.5 L HN_3 on $\text{Si}(111)\text{-}7\times 7$ dosed at 120 K and then annealed to the indicated temperatures. Solid lines are drawn through the experiment points.
- Figure 8. Molecular structure of hydrazoic acid.
- Figure 9. He II UPS results of 2.0 ± 0.5 L HN_3 on $\text{Si}(111)\text{-}7\times 7$, dosed at 120 K and then annealed to the indicated temperatures. The surface states S_1 and S_2 can be observed in the spectrum of clean $\text{Si}(111)\text{-}7\times 7$ (bottom).
- Figure 10. HREEL spectra of 2.0 ± 0.5 L HN_3 on $\text{Si}(111)\text{-}7\times 7$ and $\text{Si}(100)\text{-}2\times 1$ surfaces, dosed at 120 K and sequentially warmed to 270 K.
- Figure 11. He II UPS results of 2.0 ± 0.5 L HN_3 dosed $\text{Si}(111)\text{-}7\times 7$ and $\text{Si}(100)\text{-}2\times 1$. The lower spectrum for each surface represented the clean surface at 120 K.

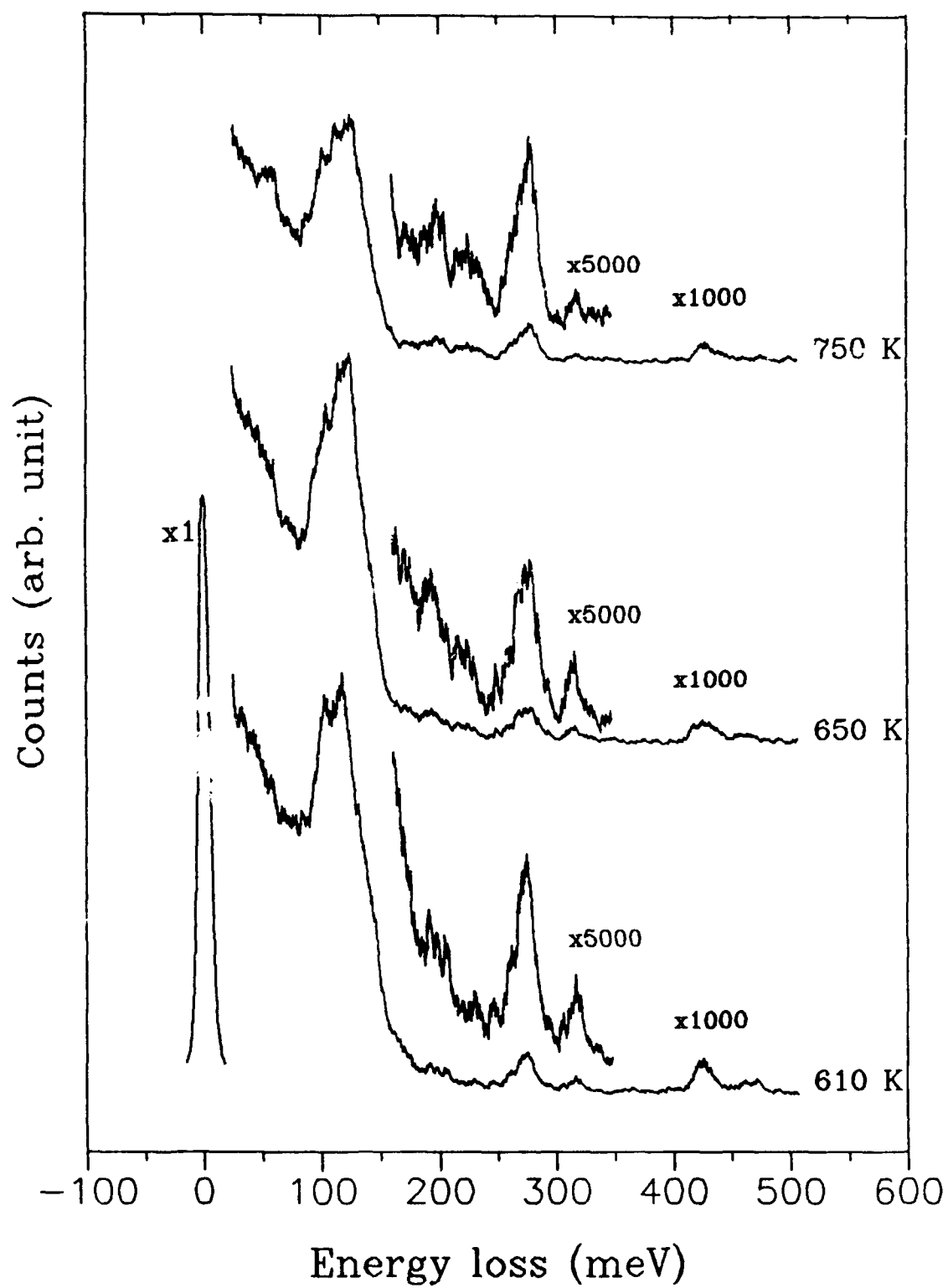


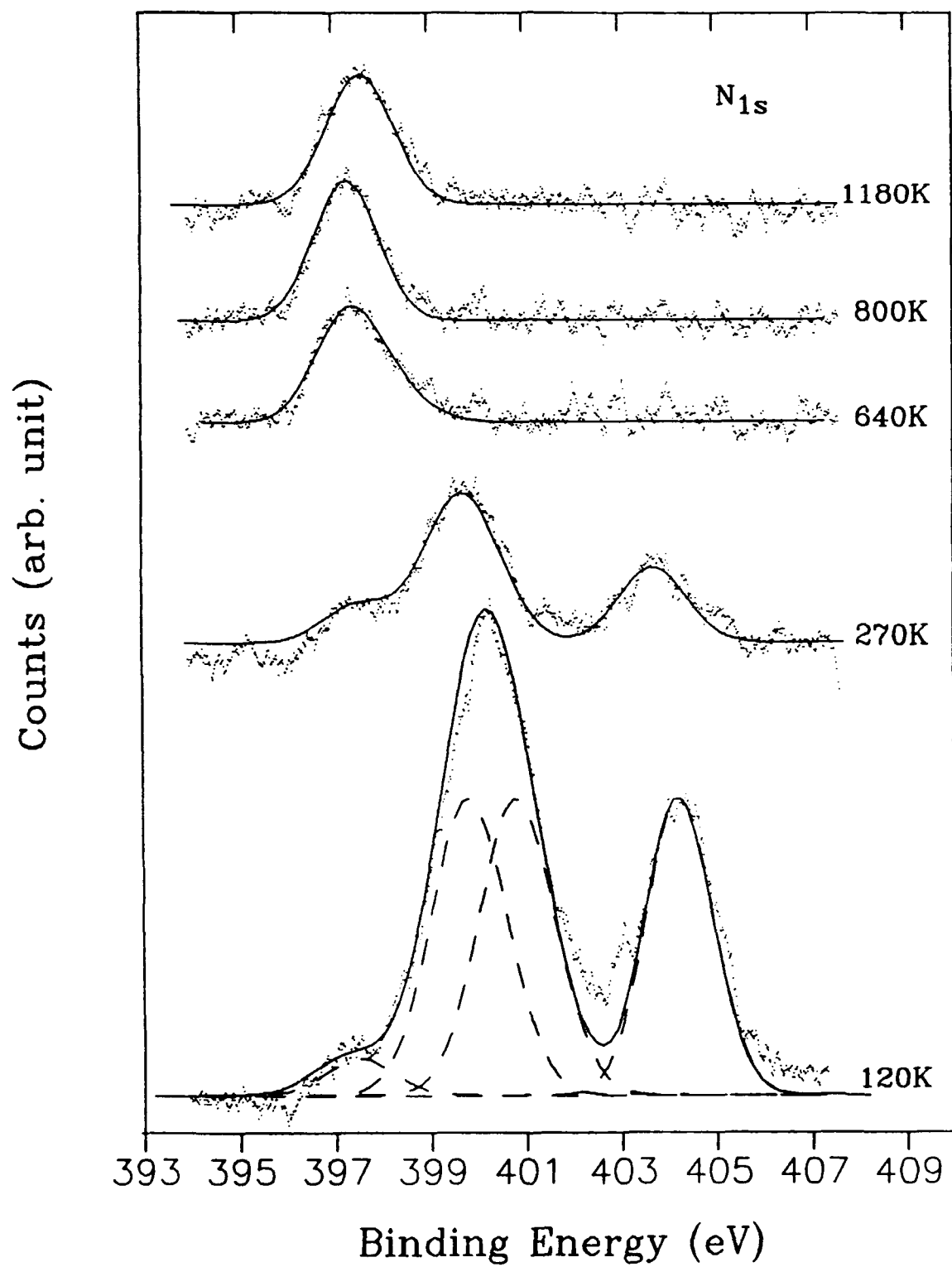


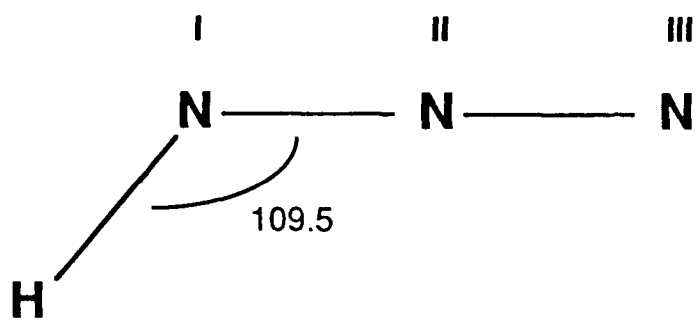












Counts (arb. units)

